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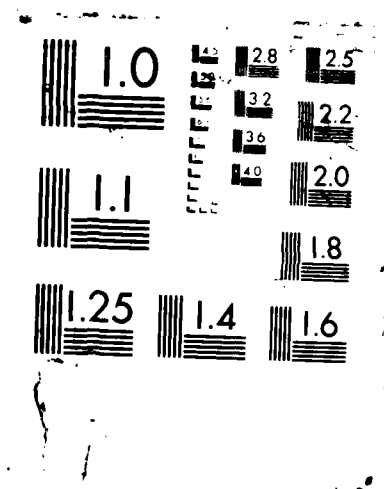
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**DETERMINATION OF AQUO-COMPLEXES OF
CHROMIUM AND IRON IN CHROMIUM PLATING AND
POLISHING SOLUTIONS BY ION CHROMATOGRAPHY**

SAMUEL SOPOK

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Aquo-complexes of chromium and iron in chromium plating and polishing solutions of individual concentration levels above 7.5 g/l result in a poor quality plate condition. An ion chromatographic procedure utilizing UV-visible and atomic absorption detection for determining 0-20 g/l concentration levels of these aquo-complexes is described. Since no derivatizations are necessary, matrix effects are much less common compared to previous chromatographic methods. The relative standard deviation is about two percent and sensitivity is about 1 ppm for these determinations.		

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INTRODUCTION

The separation and subsequent detection of aquo-complexes of chromium and iron in chromium plating and polishing solutions by ion exchange chromatography are necessary to maximize the plating quality of low alloy steels.

These aquo-complexes should not individually exceed 7.5 g/l, but may range from 0-20 g/l. The ions result from metal finishing processes such as polishing, reverse-plating, and normal plating providing Fe(II), Fe(III), and Cr(III) ions, respectively. Additional Cr(III) ions result from accidental oxidation of ethylene glycol due to coolant leaks.

Past methods (refs 1-7) have derivatized these aquo-complexes to enhance separation and detection. Such methods have included high cost-element specific atomic absorption detection (ref 1) and more practical low cost-multi-element UV-visible detection (refs 2-7).

The chemistries of these derivatizations are difficult to control when past methods are applied to chromium plating and polishing solutions. Acid strength and variability affect the derivatization chemistries causing matrix effects. The purpose of this study is to develop an ion chromatographical procedure that eliminates the derivatization chemistries, while providing an analysis range of 0-20 g/l for these aquo-complexes in chromium plating and polishing solutions.

EXPERIMENTAL PROCEDURE

The Dionex model 2020i ion chromatograph is the analysis system used. The system flowstream consists of the element reservoir (0.283 M HNO_3), element delivery system (2.3 ml/min), injector valve (500 μl loop), separator column

References are listed at the end of this report.

(Dionex HPIC-CG2), UV-visible detector (Dionex, 0.5 AUFS), and the atomic absorption detector (Perkin-Elmer, aspirator flow rate is 2.8 ml/min). Air-tight coupling of the two detectors is easily accomplished with the standard tubing provided. For aquo-complexes of iron and chromium, UV-visible detection is at 330 and 570 nm and atomic absorption detection is at 248.3 and 357.9 nm, respectively.

UV-visible wavelengths are chosen from initial spectra (300-600 nm) acquired for these aquo-complexes on a UV-visible spectrophotometer (Bausch and Lomb).

Matrix types include chromium plating (2.50 g/l H_2SO_4 and 250 g/l CrO_3) and polishing (750 g/l H_3PO_4 and 750 g/l H_2SO_4) solutions at typical operating levels. Chlorides of iron and chromium are used to prepare aquo-complex standards. Both standard and sample matrices require a 250 dilution to attain the 0-80 ppm detection range for these aquo-complexes.

The integrator (Dionex) attenuation is 16 and 256 for UV-visible and atomic detection, respectively.

RESULTS AND DISCUSSION

For UV-visible detection, it is necessary to choose wavelengths for Fe(III) and Cr(III) ions that have sufficient absorbance for detection but do not interfere with other matrix components present. For the chromium plating and polishing solution matrices, Table I illustrates that 300 nm and 570 nm are ideal for Fe(III) and Cr(III) ion detection, respectively. There is no interference if the ions elute simultaneously.

Separation of these aquo-complexes is accomplished by cation exchange chromatography using a nitric acid eluent which completely oxidizes sample Fe(II) ions to Fe(III) ions, while leaving Cr(III) ions intact.

TABLE I. UV-VISIBLE SPECTRA OF DETECTABLE COMPLEXES

Wavelength (nm)	Cr(IV) (1000 ppm)	Cr(III) (1000 ppm)	Fe(III) (1000 ppm)
325	1.90	0.03	1.50
330	1.93	0.04	1.57
350	2.00	0.08	1.70
375	2.10	0.21	1.60
400	2.00	0.33	0.73
425	1.90	0.27	0.18
450	1.60	0.14	0.04
475	0.49	0.07	0.01
500	0.08	0.09	0.00
525	0.01	0.16	0.00
550	0.00	0.24	0.00
570	0.00	0.28	0.00
575	0.00	0.29	0.00
600	0.00	0.26	0.00

Tables II through IV show linear calibration data in the concentration range of 0-80 ppm for aquo-complexes of iron and chromium after a 250 dilution of chromium plating and polishing solutions. The percent relative standard deviation and detection limit of the aquo-complex calibration data are two percent and 1 ppm, respectively. For retention times of the aquo-complexes of chromium and iron, UV-visible detection has 3.3 and 3.9 minutes and atomic absorption detection has 3.7 and 4.3 minutes, respectively. In these metal finishing solutions, unretained peaks did not affect determinations of the aquo-complexes using either detector.

TABLE II. DETERMINATION OF Cr(III) IONS IN CHROMIUM PLATING SOLUTIONS

Cr(III) (ppm)	UV-Visible Height (AU)	Atomic Absorption Height (AU)
20	0.053	0.051
40	0.105	0.100
60	0.157	0.150
80	0.215	0.199

TABLE III. DETERMINATION OF Fe(III) IONS IN CHROMIUM PLATING SOLUTIONS

Fe(III) (ppm)	UV-Visible Height (AU)	Atomic Absorption Height (AU)
20	0.063	0.045
40	0.122	0.085
60	0.184	0.129
80	0.243	0.171

TABLE IV. DETERMINATION OF Fe(II) IONS IN CHROMIUM POLISHING SOLUTIONS

Fe(II) (ppm)	UV-Visible Height (AU)	Atomic Absorption Height (AU)
20	0.066	0.038
40	0.126	0.077
60	0.192	0.118
80	0.266	0.147

Ion chromatography, without derivatization, is an effective method for the determination of aquo-complexes of chromium and iron in chromium plating and polishing solutions for low alloy steels. This method can be applied to other chemical matrices with proper precautions.

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